



## Octarubidium di-mu-sulfato-kappa O-4:O '-bis[cis-dioxido-cis-disulfatotungstate(VI)]

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# Octarubidium di- $\mu$ -sulfato- $\kappa^4$ O:O'-bis-[cis-dioxido-cis-disulfatotungstate(VI)]

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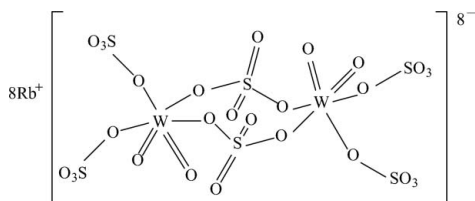
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Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{S-O}) = 0.003$  Å;  $R$  factor = 0.020;  $wR$  factor = 0.052; data-to-parameter ratio = 17.5.

The title compound,  $\text{Rb}_8[\text{W}_2\text{O}_4(\text{SO}_4)_6]$ , was precipitated from a melt of tungsten(VI) oxide and rubidium sulfate in rubidium disulfate. The unit cell contains two discrete  $[\{\text{W}^{\text{VI}}\text{O}_2(\text{SO}_4)_2\}_2(\mu\text{-SO}_4)_2]^{8-}$  units connected by Rb–O coordination. The W atom is octahedrally surrounded by two oxide ligands, two terminal sulfate ligands and two bridging sulfate groups. One Rb atom is coordinated by eight O atoms, whereas the three other Rb atoms are coordinated by nine O atoms from sulfate and oxide groups, leading to distorted  $[\text{RbO}_x]$  polyhedra.

## Related literature

For methods used in the synthesis, see: Berg *et al.* (2006); Borup *et al.* (1990); Nørbygaard *et al.* (1998). For the crystal structure of the potassium analog, see: Schäffer & Berg (2005).



## Experimental

### Crystal data

$\text{Rb}_8[\text{W}_2\text{O}_4(\text{SO}_4)_6]$   
 $M_r = 1691.86$   
 Monoclinic,  $P2_1/n$   
 $a = 9.6405$  (5) Å  
 $b = 13.9890$  (7) Å  
 $c = 10.7692$  (5) Å  
 $\beta = 90.472$  (1)°

$V = 1452.30$  (12) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 21.77$  mm<sup>-1</sup>  
 $T = 120$  K  
 $0.45 \times 0.20 \times 0.05$  mm

### Data collection

Bruker SMART APEX  
 diffractometer

Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2002)  
 $T_{\min} = 0.077$ ,  $T_{\max} = 0.59$

18895 measured reflections  
 3496 independent reflections

3360 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.036$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.052$   
 $S = 1.11$   
 3496 reflections

200 parameters  
 $\Delta\rho_{\text{max}} = 1.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.51$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

W1—O1	1.716 (2)	Rb3—O12 <sup>i</sup>	3.101 (2)
W1—O2	1.721 (2)	Rb3—O11 <sup>vii</sup>	3.170 (2)
W1—O3	1.960 (2)	Rb3—O12 <sup>v</sup>	3.173 (3)
W1—O4	2.009 (2)	Rb3—O1	3.220 (2)
W1—O5	2.097 (2)	Rb3—O13 <sup>v</sup>	3.225 (3)
W1—O6	2.254 (2)	Rb4—O8 <sup>viii</sup>	2.910 (3)
Rb1—O1	2.877 (2)	Rb4—O3 <sup>i</sup>	2.914 (2)
Rb1—O8	2.931 (2)	Rb4—O10	2.941 (3)
Rb1—O7	2.939 (3)	Rb4—O14	2.964 (2)
Rb1—O9 <sup>j</sup>	2.955 (3)	Rb4—O13 <sup>i</sup>	2.981 (3)
Rb1—O6 <sup>ii</sup>	3.009 (2)	Rb4—O12 <sup>i</sup>	3.103 (3)
Rb1—O11 <sup>iii</sup>	3.010 (2)	Rb4—O6 <sup>i</sup>	3.221 (2)
Rb1—O2 <sup>iii</sup>	3.084 (2)	Rb4—O5	3.253 (2)
Rb1—O5 <sup>ii</sup>	3.185 (2)	Rb4—O4	3.423 (2)
Rb2—O14 <sup>iv</sup>	2.761 (3)	S1—O11	1.445 (2)
Rb2—O7 <sup>v</sup>	2.893 (2)	S1—O14	1.449 (2)
Rb2—O9 <sup>vi</sup>	2.903 (3)	S1—O6 <sup>ix</sup>	1.490 (2)
Rb2—O2	2.939 (3)	S1—O4	1.531 (2)
Rb2—O13 <sup>ii</sup>	2.986 (2)	S2—O12	1.451 (3)
Rb2—O8	3.082 (3)	S2—O9	1.452 (3)
Rb2—O10 <sup>v</sup>	3.106 (3)	S2—O8	1.454 (3)
Rb2—O9	3.337 (3)	S2—O3	1.575 (2)
Rb2—O1	3.374 (3)	S3—O13	1.461 (2)
Rb3—O11	2.776 (2)	S3—O7	1.464 (3)
Rb3—O10 <sup>ii</sup>	2.788 (3)	S3—O10	1.464 (3)
Rb3—O7 <sup>v</sup>	2.874 (2)	S3—O5	1.528 (2)
Rb3—O14 <sup>vii</sup>	2.935 (2)		

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iv)  $x + 1, y, z$ ; (v)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (vi)  $-x + 1, -y, -z + 2$ ; (vii)  $-x, -y, -z + 1$ ; (viii)  $x - 1, y, z$ ; (ix)  $-x, -y, -z + 2$ .

Data collection: SMART (Bruker, 2002); cell refinement: SAINT-Plus (Bruker, 2002); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: ORTEP-3 (Farrugia, 1997) and ATOMS (Dowty, 2000); software used to prepare material for publication: SHELXTL.

The authors thank Astrid Schöneberg and Bodil Holten for technical assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2090).

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**supplementary materials**

*Acta Cryst.* (2009). E65, i88 [ doi:10.1107/S1600536809046431 ]

# Octarubidium di- $\mu$ -sulfato- $\kappa^4 O:O'$ -bis[*cis*-dioxido-*cis*-disulfatotungstate(VI)]

K. Ståhl and R. W. Berg

## Comment

Tungsten trioxide is known as a highly inert solid, practically insoluble in acids. It was discovered that  $WO_3$  can be dissolved in considerable amounts in acidic sulfate melts at high temperatures (Schäffer and Berg, 2005 and Berg *et al.*, 2006). When therefore  $WO_3$ ,  $Rb_2SO_4$  and  $Rb_2S_2O_7$  are mixed in varying molar amounts in sealed ampoules and heated for equilibration in a rocking furnace at appr. 600 °C for appr. 1 hr, clear melts are formed ( $Rb_2S_2O_7$  is hygroscopic and needs to be handled in a dry box). It has been shown that  $[WO_2]^{2+}$  ions formed are solvated by  $SO_4^{2-}$  ions. The stoichiometry of the reaction have been determined fairly accurately as 1:1:1, or  $2WO_3 + 2M_2SO_4 + 2M_2S_2O_7 \rightarrow M_8[(WO_2)_2(\mu-SO_4)_2(SO_4)_4]$  for the case of  $M = K$ , Schäffer and Berg, 2005. Here we have studied the case of  $M = Rb$  and have found closely analogous results for single crystals of the compound,  $1WO_3:1Rb_2S_2O_7:1Rb_2SO_4$ . The main difference for  $M = Rb$  as compared to  $M = K$  is as expected in the  $M - O$  coordination: Rb1/K1, CN = 8/8,  $\langle M - O \rangle = 2.999$  (1)/2.822 (1); Rb2/K2, CN = 9/7,  $\langle M - O \rangle = 3.042$  (1)/2.825 (1); Rb3/K3, CN = 9/8,  $\langle M - O \rangle = 3.029$  (1)/2.909 (1); Rb4/K4, CN = 9/9,  $\langle M - O \rangle = 3.079$  (1)/2.945 (1). As the oxo-sulfatotungstate groups are extended in the b-direction, the major changes in the unit cell axes are observed in the a- and c- directions.

## Experimental

The crystals were grown from a melt of 20.6 mol % tungsten trioxide and 19.9 mol % rubidium sulfate in rubidium disulfate, using the methods described by Borup *et al.* (1990), Nørbygaard *et al.* (1998) and Berg *et al.* (2006).

## Figures

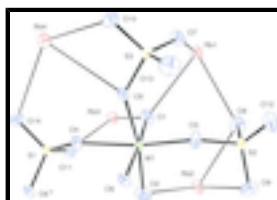


Fig. 1. The asymmetric unit of (I) showing 50% probability displacement ellipsoids and the atomic numbering.  $O6^{IV}$  was added to complete the S1 coordination.

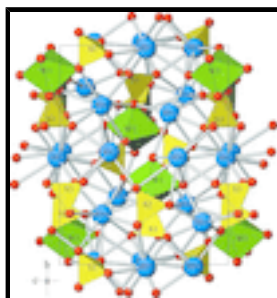


Fig. 2. The crystal packing of (I) viewed down the  $a$  axis. W atoms are in the centers of the octahedra and S atoms are in the centers of the tetrahedra. Rb are shown as large and O as small spheres.

## Octarubidium di- $\mu$ -sulfato- $\kappa^4 O:O'$ -bis[*cis*-dioxido-*cis*-disulfatotungstate(VI)]

### Crystal data

Rb <sub>8</sub> [W <sub>2</sub> O <sub>4</sub> (SO <sub>4</sub> ) <sub>6</sub> ]	$F_{000} = 1528$
$M_r = 1691.86$	$D_x = 3.869 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: -P 2yn	Cell parameters from 6979 reflections
$a = 9.6405 (5) \text{ \AA}$	$\theta = 2.4\text{--}28.0^\circ$
$b = 13.9890 (7) \text{ \AA}$	$\mu = 21.77 \text{ mm}^{-1}$
$c = 10.7692 (5) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 90.4720 (10)^\circ$	Irregular, colourless
$V = 1452.30 (12) \text{ \AA}^3$	$0.45 \times 0.20 \times 0.05 \text{ mm}$
$Z = 2$	

### Data collection

Bruker SMART APEX diffractometer	3496 independent reflections
Radiation source: fine-focus sealed tube	3360 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.036$
$T = 120 \text{ K}$	$\theta_{\text{max}} = 28.0^\circ$
$\omega$ scan, frame data integration	$\theta_{\text{min}} = 2.4^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$h = -12 \rightarrow 12$
$T_{\text{min}} = 0.077$ , $T_{\text{max}} = 0.59$	$k = -18 \rightarrow 18$
18895 measured reflections	$l = -14 \rightarrow 14$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 1.1918P]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.052$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 1.35 \text{ e \AA}^{-3}$
3496 reflections	$\Delta\rho_{\text{min}} = -1.51 \text{ e \AA}^{-3}$
200 parameters	Extinction correction: SHELXTL (Sheldrick, 2008),
Primary atom site location: structure-invariant direct methods	$F_c^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00175 (10)

### Special details

**Experimental.** Oxford Cryosystem liquid nitrogen cryostream cooler

**Geometry.** All e.s.d.'s are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry.

**Refinement.** A series of identical frames was collected twice during the experiment to monitor decay. No decay was detected and decay correction was not applied. Systematic conditions suggested the unambiguous space group. The structure was solved by direct methods (Sheldrick, 2008). The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on  $F^2$  (Sheldrick, 2008). Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger. The highest peak in the final difference Fourier map was 0.85 Å and the deepest hole was 0.78 Å from W1. The final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
W1	0.168190 (12)	0.117132 (8)	0.917586 (11)	0.00604 (6)
Rb1	0.31202 (3)	0.30953 (2)	0.65221 (3)	0.01095 (8)
Rb2	0.50882 (3)	0.01145 (2)	0.79641 (3)	0.01149 (8)
Rb3	0.19055 (3)	0.01388 (2)	0.51347 (3)	0.01057 (8)
Rb4	−0.23085 (3)	0.22589 (2)	0.74755 (3)	0.01173 (8)
S1	−0.07712 (8)	−0.01972 (5)	0.80402 (7)	0.00671 (15)
S2	0.46037 (8)	0.22894 (6)	0.97953 (7)	0.00823 (15)
S3	0.03580 (8)	0.34141 (5)	0.94629 (7)	0.00726 (15)
O1	0.2116 (3)	0.13695 (17)	0.7656 (2)	0.0126 (5)
O2	0.2550 (3)	0.01169 (17)	0.9456 (2)	0.0134 (5)
O3	0.3015 (2)	0.20560 (17)	0.9939 (2)	0.0105 (5)
O4	−0.0203 (2)	0.06004 (16)	0.8874 (2)	0.0095 (4)
O5	0.0314 (2)	0.23235 (16)	0.9395 (2)	0.0113 (5)
O6	0.0953 (2)	0.10525 (15)	1.1153 (2)	0.0086 (4)
O7	0.1394 (3)	0.37617 (16)	0.8585 (2)	0.0123 (5)
O8	0.4896 (3)	0.22782 (18)	0.8473 (2)	0.0146 (5)
O9	0.5342 (3)	0.1533 (2)	1.0446 (3)	0.0221 (6)
O10	−0.1042 (3)	0.37142 (17)	0.9097 (2)	0.0143 (5)
O11	0.0230 (3)	−0.04158 (17)	0.7090 (2)	0.0118 (5)
O12	0.4761 (3)	0.32204 (18)	1.0374 (2)	0.0160 (5)
O13	0.0695 (3)	0.36869 (18)	1.0740 (2)	0.0168 (5)
O14	−0.2088 (3)	0.01462 (17)	0.7559 (2)	0.0121 (5)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
W1	0.00608 (8)	0.00633 (8)	0.00575 (8)	−0.00051 (4)	0.00225 (5)	−0.00028 (4)
Rb1	0.01021 (15)	0.01196 (15)	0.01072 (15)	−0.00113 (11)	0.00177 (11)	0.00109 (11)
Rb2	0.01089 (16)	0.01125 (15)	0.01242 (16)	−0.00146 (11)	0.00470 (11)	−0.00220 (11)
Rb3	0.01010 (15)	0.01395 (15)	0.00769 (15)	−0.00045 (11)	0.00251 (11)	0.00227 (10)
Rb4	0.01259 (16)	0.01381 (15)	0.00883 (15)	−0.00152 (12)	0.00221 (11)	−0.00042 (11)

## supplementary materials

S1	0.0069 (3)	0.0080 (3)	0.0052 (3)	−0.0015 (3)	0.0008 (3)	0.0002 (3)
S2	0.0065 (3)	0.0102 (4)	0.0080 (4)	−0.0011 (3)	0.0004 (3)	0.0005 (3)
S3	0.0086 (4)	0.0070 (3)	0.0062 (3)	0.0008 (3)	0.0016 (3)	−0.0007 (3)
O1	0.0157 (12)	0.0143 (11)	0.0077 (11)	−0.0046 (10)	0.0025 (9)	−0.0001 (9)
O2	0.0144 (12)	0.0098 (11)	0.0161 (12)	0.0047 (9)	0.0057 (9)	0.0011 (9)
O3	0.0071 (11)	0.0141 (11)	0.0104 (11)	−0.0017 (9)	0.0015 (8)	−0.0033 (9)
O4	0.0099 (11)	0.0093 (10)	0.0094 (11)	−0.0024 (9)	0.0007 (8)	−0.0019 (8)
O5	0.0088 (11)	0.0081 (10)	0.0170 (12)	0.0002 (9)	0.0006 (9)	0.0009 (9)
O6	0.0110 (11)	0.0068 (10)	0.0080 (11)	−0.0025 (8)	0.0025 (9)	0.0006 (8)
O7	0.0123 (12)	0.0127 (12)	0.0120 (12)	−0.0024 (9)	0.0043 (9)	0.0030 (8)
O8	0.0156 (12)	0.0178 (12)	0.0105 (12)	−0.0028 (10)	0.0057 (9)	−0.0012 (9)
O9	0.0171 (13)	0.0202 (14)	0.0288 (15)	0.0015 (11)	−0.0074 (11)	0.0102 (11)
O10	0.0099 (12)	0.0123 (11)	0.0207 (14)	0.0039 (9)	0.0018 (10)	−0.0009 (9)
O11	0.0142 (12)	0.0130 (11)	0.0084 (11)	−0.0017 (9)	0.0049 (8)	−0.0008 (9)
O12	0.0153 (12)	0.0157 (12)	0.0170 (13)	−0.0054 (10)	0.0020 (10)	−0.0047 (10)
O13	0.0250 (15)	0.0173 (12)	0.0079 (12)	0.0004 (11)	−0.0014 (10)	−0.0039 (9)
O14	0.0110 (12)	0.0151 (12)	0.0102 (11)	0.0011 (9)	−0.0017 (9)	0.0014 (9)

### *Geometric parameters (Å, °)*

W1—O1	1.716 (2)	Rb3—O12 <sup>i</sup>	3.101 (2)
W1—O2	1.721 (2)	Rb3—O11 <sup>vii</sup>	3.170 (2)
W1—O3	1.960 (2)	Rb3—O12 <sup>v</sup>	3.173 (3)
W1—O4	2.009 (2)	Rb3—O1	3.220 (2)
W1—O5	2.097 (2)	Rb3—O13 <sup>v</sup>	3.225 (3)
W1—O6	2.254 (2)	Rb4—O8 <sup>viii</sup>	2.910 (3)
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Rb3—O11	2.776 (2)	S3—O7	1.464 (3)
Rb3—O10 <sup>ii</sup>	2.788 (3)	S3—O10	1.464 (3)

Rb3—O7 <sup>v</sup>	2.874 (2)	S3—O5	1.528 (2)
Rb3—O14 <sup>vii</sup>	2.935 (2)		
O1—W1—O2	100.59 (12)	O7 <sup>v</sup> —Rb3—O12 <sup>i</sup>	146.54 (7)
O1—W1—O3	97.67 (11)	O14 <sup>vii</sup> —Rb3—O12 <sup>i</sup>	103.19 (7)
O2—W1—O3	98.71 (11)	O11—Rb3—O11 <sup>vii</sup>	103.26 (6)
O1—W1—O4	97.90 (10)	O10 <sup>ii</sup> —Rb3—O11 <sup>vii</sup>	94.90 (7)
O2—W1—O4	97.20 (11)	O7 <sup>v</sup> —Rb3—O11 <sup>vii</sup>	143.97 (6)
O3—W1—O4	155.24 (9)	O14 <sup>vii</sup> —Rb3—O11 <sup>vii</sup>	46.63 (6)
O1—W1—O5	98.15 (11)	O12 <sup>i</sup> —Rb3—O11 <sup>vii</sup>	62.82 (6)
O2—W1—O5	160.75 (11)	O11—Rb3—O12 <sup>v</sup>	66.26 (7)
O3—W1—O5	83.02 (9)	O10 <sup>ii</sup> —Rb3—O12 <sup>v</sup>	141.04 (7)
O4—W1—O5	75.81 (9)	O7 <sup>v</sup> —Rb3—O12 <sup>v</sup>	78.58 (6)
O1—W1—O6	173.62 (10)	O14 <sup>vii</sup> —Rb3—O12 <sup>v</sup>	75.47 (7)
O2—W1—O6	85.75 (10)	O12 <sup>i</sup> —Rb3—O12 <sup>v</sup>	107.66 (6)
O3—W1—O6	81.90 (9)	O11 <sup>vii</sup> —Rb3—O12 <sup>v</sup>	69.40 (6)
O4—W1—O6	80.50 (9)	O11—Rb3—O1	62.79 (7)
O5—W1—O6	75.48 (9)	O10 <sup>ii</sup> —Rb3—O1	89.42 (7)
O1—Rb1—O8	64.22 (7)	O7 <sup>v</sup> —Rb3—O1	85.54 (6)
O1—Rb1—O7	75.57 (7)	O14 <sup>vii</sup> —Rb3—O1	154.44 (7)
O8—Rb1—O7	84.99 (7)	O12 <sup>i</sup> —Rb3—O1	64.64 (6)
O1—Rb1—O9 <sup>i</sup>	90.40 (8)	O11 <sup>vii</sup> —Rb3—O1	127.46 (6)
O8—Rb1—O9 <sup>i</sup>	150.64 (8)	O12 <sup>v</sup> —Rb3—O1	128.76 (6)
O7—Rb1—O9 <sup>i</sup>	73.96 (7)	O11—Rb3—O13 <sup>v</sup>	117.97 (7)
O1—Rb1—O6 <sup>ii</sup>	134.22 (7)	O10 <sup>ii</sup> —Rb3—O13 <sup>v</sup>	74.48 (7)
O8—Rb1—O6 <sup>ii</sup>	73.97 (7)	O7 <sup>v</sup> —Rb3—O13 <sup>v</sup>	46.39 (7)
O7—Rb1—O6 <sup>ii</sup>	119.62 (6)	O14 <sup>vii</sup> —Rb3—O13 <sup>v</sup>	64.96 (6)
O9 <sup>i</sup> —Rb1—O6 <sup>ii</sup>	134.35 (7)	O12 <sup>i</sup> —Rb3—O13 <sup>v</sup>	166.10 (7)
O1—Rb1—O11 <sup>iii</sup>	123.25 (6)	O11 <sup>vii</sup> —Rb3—O13 <sup>v</sup>	108.61 (6)
O8—Rb1—O11 <sup>iii</sup>	67.10 (7)	O12 <sup>v</sup> —Rb3—O13 <sup>v</sup>	77.31 (7)
O7—Rb1—O11 <sup>iii</sup>	72.87 (7)	O1—Rb3—O13 <sup>v</sup>	122.86 (6)
O9 <sup>i</sup> —Rb1—O11 <sup>iii</sup>	123.13 (7)	O8 <sup>viii</sup> —Rb4—O3 <sup>i</sup>	116.73 (7)
O6 <sup>ii</sup> —Rb1—O11 <sup>iii</sup>	46.76 (6)	O8 <sup>viii</sup> —Rb4—O10	98.95 (7)
O1—Rb1—O2 <sup>iii</sup>	147.59 (7)	O3 <sup>i</sup> —Rb4—O10	106.38 (7)
O8—Rb1—O2 <sup>iii</sup>	136.20 (7)	O8 <sup>viii</sup> —Rb4—O14	93.69 (7)
O7—Rb1—O2 <sup>iii</sup>	81.33 (6)	O3 <sup>i</sup> —Rb4—O14	110.37 (7)
O9 <sup>i</sup> —Rb1—O2 <sup>iii</sup>	61.21 (7)	O10—Rb4—O14	130.00 (7)
O6 <sup>ii</sup> —Rb1—O2 <sup>iii</sup>	77.25 (6)	O8 <sup>viii</sup> —Rb4—O13 <sup>i</sup>	68.94 (7)
O11 <sup>iii</sup> —Rb1—O2 <sup>iii</sup>	69.12 (6)	O3 <sup>i</sup> —Rb4—O13 <sup>i</sup>	68.39 (7)
O1—Rb1—O5 <sup>ii</sup>	112.24 (7)	O10—Rb4—O13 <sup>i</sup>	160.41 (7)
O8—Rb1—O5 <sup>ii</sup>	93.25 (6)	O14—Rb4—O13 <sup>i</sup>	67.81 (7)
O7—Rb1—O5 <sup>ii</sup>	170.30 (6)	O8 <sup>viii</sup> —Rb4—O12 <sup>i</sup>	150.99 (7)



## supplementary materials

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O9 <sup>i</sup> —Rb1—O5 <sup>ii</sup>	110.80 (7)	O3 <sup>i</sup> —Rb4—O12 <sup>i</sup>	46.59 (6)
O6 <sup>ii</sup> —Rb1—O5 <sup>ii</sup>	50.90 (6)	O10—Rb4—O12 <sup>i</sup>	108.45 (7)
O11 <sup>iii</sup> —Rb1—O5 <sup>ii</sup>	97.65 (6)	O14—Rb4—O12 <sup>i</sup>	76.14 (7)
O2 <sup>iii</sup> —Rb1—O5 <sup>ii</sup>	93.51 (6)	O13 <sup>i</sup> —Rb4—O12 <sup>i</sup>	82.09 (7)
O14 <sup>iv</sup> —Rb2—O7 <sup>v</sup>	113.73 (7)	O8 <sup>viii</sup> —Rb4—O6 <sup>i</sup>	71.11 (7)
O14 <sup>iv</sup> —Rb2—O9 <sup>vi</sup>	104.59 (7)	O3 <sup>i</sup> —Rb4—O6 <sup>i</sup>	53.40 (6)
O7 <sup>v</sup> —Rb2—O9 <sup>vi</sup>	75.43 (7)	O10—Rb4—O6 <sup>i</sup>	88.10 (6)
O14 <sup>iv</sup> —Rb2—O2	155.92 (7)	O14—Rb4—O6 <sup>i</sup>	141.38 (6)
O7 <sup>v</sup> —Rb2—O2	84.64 (7)	O13 <sup>i</sup> —Rb4—O6 <sup>i</sup>	73.59 (6)
O9 <sup>vi</sup> —Rb2—O2	63.56 (7)	O12 <sup>i</sup> —Rb4—O6 <sup>i</sup>	99.87 (6)
O14 <sup>iv</sup> —Rb2—O13 <sup>ii</sup>	70.38 (7)	O8 <sup>viii</sup> —Rb4—O5	118.84 (7)
O7 <sup>v</sup> —Rb2—O13 <sup>ii</sup>	90.22 (7)	O3 <sup>i</sup> —Rb4—O5	119.85 (6)
O9 <sup>vi</sup> —Rb2—O13 <sup>ii</sup>	161.61 (8)	O10—Rb4—O5	44.51 (6)
O2—Rb2—O13 <sup>ii</sup>	127.42 (7)	O14—Rb4—O5	87.33 (6)
O14 <sup>iv</sup> —Rb2—O8	94.19 (7)	O13 <sup>i</sup> —Rb4—O5	154.80 (6)
O7 <sup>v</sup> —Rb2—O8	135.64 (7)	O12 <sup>i</sup> —Rb4—O5	88.19 (6)
O9 <sup>vi</sup> —Rb2—O8	131.74 (8)	O6 <sup>i</sup> —Rb4—O5	131.24 (6)
O2—Rb2—O8	81.38 (7)	O8 <sup>viii</sup> —Rb4—O4	113.04 (6)
O13 <sup>ii</sup> —Rb2—O8	66.65 (7)	O3 <sup>i</sup> —Rb4—O4	124.58 (6)
O14 <sup>iv</sup> —Rb2—O10 <sup>v</sup>	66.37 (7)	O10—Rb4—O4	88.06 (6)
O7 <sup>v</sup> —Rb2—O10 <sup>v</sup>	47.37 (7)	O14—Rb4—O4	43.02 (6)
O9 <sup>vi</sup> —Rb2—O10 <sup>v</sup>	88.01 (8)	O13 <sup>i</sup> —Rb4—O4	110.63 (6)
O2—Rb2—O10 <sup>v</sup>	130.12 (7)	O12 <sup>i</sup> —Rb4—O4	77.99 (6)
O13 <sup>ii</sup> —Rb2—O10 <sup>v</sup>	73.72 (7)	O6 <sup>i</sup> —Rb4—O4	174.76 (6)
O8—Rb2—O10 <sup>v</sup>	139.93 (7)	O5—Rb4—O4	44.32 (5)
O14 <sup>iv</sup> —Rb2—O9	92.92 (7)	O11—S1—O14	113.92 (14)
O7 <sup>v</sup> —Rb2—O9	152.12 (7)	O11—S1—O6 <sup>ix</sup>	108.97 (14)
O9 <sup>vi</sup> —Rb2—O9	90.56 (7)	O14—S1—O6 <sup>ix</sup>	111.57 (14)
O2—Rb2—O9	67.50 (7)	O11—S1—O4	109.38 (14)
O13 <sup>ii</sup> —Rb2—O9	107.16 (7)	O14—S1—O4	106.03 (14)
O8—Rb2—O9	43.73 (6)	O6 <sup>ix</sup> —S1—O4	106.66 (13)
O10 <sup>v</sup> —Rb2—O9	158.07 (7)	O12—S2—O9	113.40 (16)
O14 <sup>iv</sup> —Rb2—O1	144.45 (6)	O12—S2—O8	114.19 (15)
O7 <sup>v</sup> —Rb2—O1	82.45 (6)	O9—S2—O8	111.50 (16)
O9 <sup>vi</sup> —Rb2—O1	110.23 (7)	O12—S2—O3	104.03 (14)
O2—Rb2—O1	48.93 (6)	O9—S2—O3	105.97 (15)
O13 <sup>ii</sup> —Rb2—O1	78.50 (7)	O8—S2—O3	106.88 (13)
O8—Rb2—O1	56.93 (6)	O13—S3—O7	111.90 (16)
O10 <sup>v</sup> —Rb2—O1	120.93 (6)	O13—S3—O10	112.06 (16)
O9—Rb2—O1	79.98 (6)	O7—S3—O10	111.32 (15)
O11—Rb3—O10 <sup>ii</sup>	152.16 (7)	O13—S3—O5	108.18 (14)

O11—Rb3—O7 <sup>v</sup>	77.41 (7)	O7—S3—O5	108.64 (14)
O10 <sup>ii</sup> —Rb3—O7 <sup>v</sup>	100.02 (7)	O10—S3—O5	104.36 (14)
O11—Rb3—O14 <sup>vii</sup>	138.78 (7)	S2—O3—W1	136.45 (14)
O10 <sup>ii</sup> —Rb3—O14 <sup>vii</sup>	68.51 (7)	S1—O4—W1	134.71 (14)
O7 <sup>v</sup> —Rb3—O14 <sup>vii</sup>	110.14 (7)	S3—O5—W1	139.07 (14)
O11—Rb3—O12 <sup>i</sup>	75.60 (7)	S1 <sup>ix</sup> —O6—W1	130.47 (13)
O10 <sup>ii</sup> —Rb3—O12 <sup>i</sup>	94.76 (7)		

Symmetry codes: (i)  $x-1/2, -y+1/2, z-1/2$ ; (ii)  $x+1/2, -y+1/2, z-1/2$ ; (iii)  $-x+1/2, y+1/2, -z+3/2$ ; (iv)  $x+1, y, z$ ; (v)  $-x+1/2, y-1/2, -z+3/2$ ; (vi)  $-x+1, -y, -z+2$ ; (vii)  $-x, -y, -z+1$ ; (viii)  $x-1, y, z$ ; (ix)  $-x, -y, -z+2$ .

Fig. 1

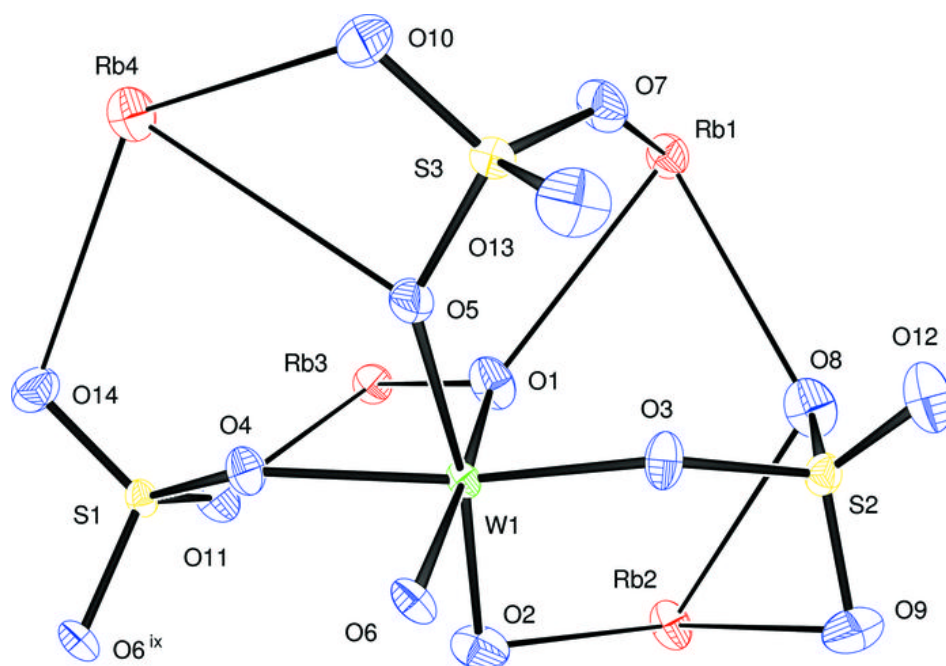


Fig. 2

